

NOTICE

The invention disclosed in this document resulted from research in aeronautical and space activities performed under programs of the National Aeronautics and Space Administration. The invention is owned by NASA and is, therefore, available for licensing in accordance with the NASA Patent Licensing Regulation (14 Code of Federal Regulations 1245.2).

To encourage commercial utilization of NASA-owned inventions, it is NASA policy to grant licenses to commercial concerns. Although NASA encourages nonexclusive licensing to promote competition and achieve the widest possible utilization, NASA will consider the granting of a limited exclusive license, pursuant to the NASA Patent Licensing Regulations, when such a license will provide the necessary incentive to the licensee to achieve early practical application of the invention.

Address inquiries and all applications for license for this invention to NASA Patent Counsel, NASA Pasadena Office, Mail Code I, 4800 Oak Grove Drive, Pasadena, California, 91103. Approved NASA forms for application for nonexclusive or exclusive license are available from the above address.

AWARDS ABSTRACT

Inventors: Walter Braun
Norman C. Peterson
Arnold M. Bass
Michael J. Kurylo III

NASA Case NO. HQN-10756-1

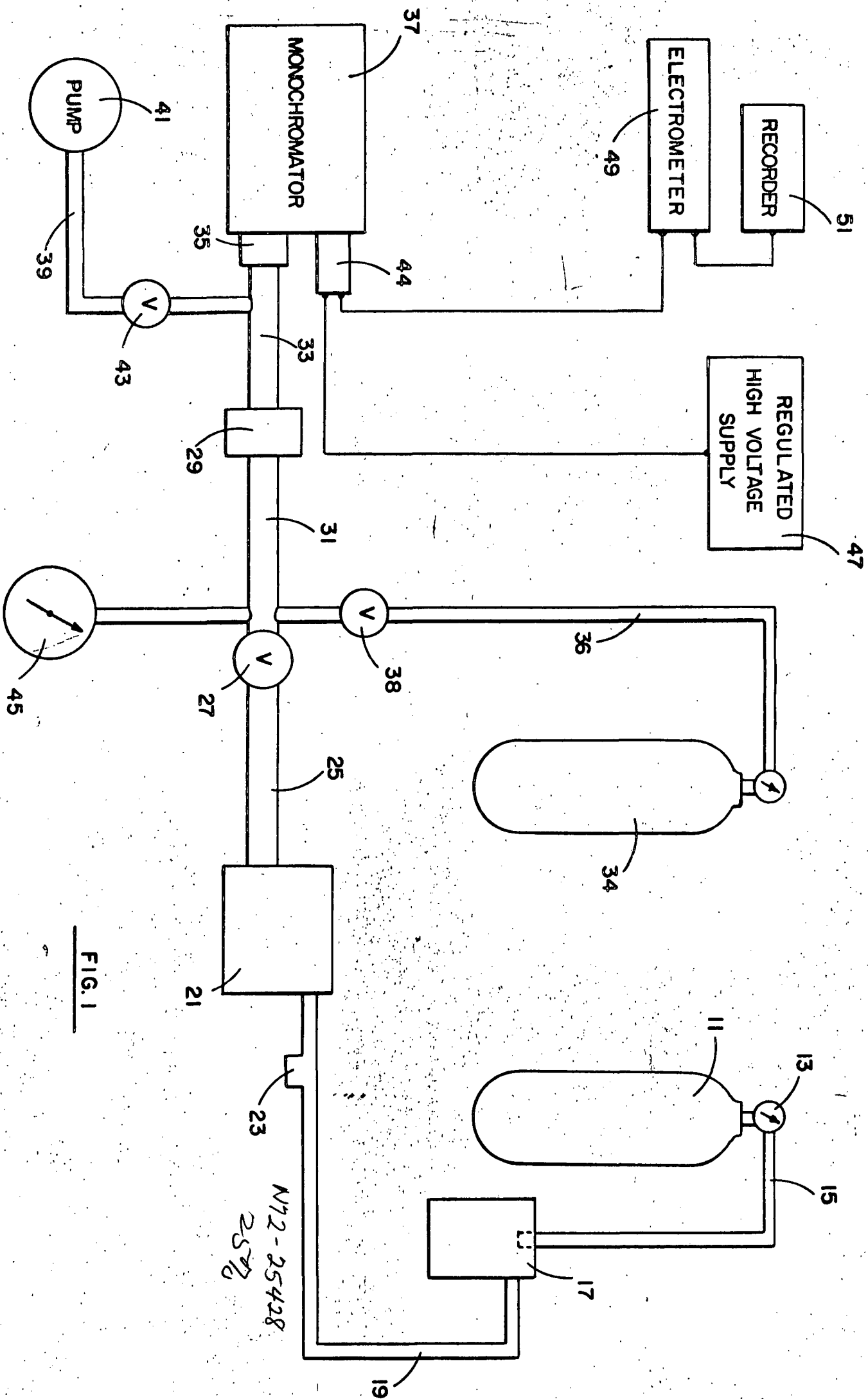
ULTRAVIOLET ATOMIC EMISSION DETECTOR

This invention relates to an apparatus and method for the quantitative and qualitative analysis of compounds containing carbon, nitrogen, and sulfur particularly. Prior to the herein invention, atomic and molecular emission detection was widely used in gas chromatographic applications. The output of a gas chromatographic column was directed to a discharge area. In the discharge area, the compound present in the effluent from the chromatographic column was fragmented by electron bombardment and by collision processes. Emission from the species were isolated by a means of a monochromator and used to detect the presence of a compound in the effluent gas stream. In the prior art approaches, high gas pressure was utilized to analyze for compounds as compared to the analysis of particular elements in compounds. Such prior methods relied upon chemical reactions to transpire which produced compounds that were observable, particularly in the visible and near-visible ultraviolet region. Such methods were thus not able to make linear quantitative analyses of elements, particularly because of the reliance upon such chemical reactions.

The objects of the present invention are accomplished by utilizing a low pressure system in combination with a vacuum UV chromatographic detector. A low pressure carrier gas, such as helium, is directed from a storage tank 11 through a trap 17 into line 19. A sample to be analyzed is emitted into the carrier gas through port 23. The carrier gas and sample are then directed to either an exponential dilutor 21, which is utilized when calibrating this system, or a gas chromatographic column when a normal sample is being run through the device. The output from the dilutor or chromatographic column 21 is then directed through line 25 and controlled by valve 27 prior to being admitted to line 31 and in turn to a microwave cavity 29, in which the gas is excited. The excited gas in the microwave cavity then is directed through line 33 to a window 35 of a UV vacuum monochromator. A pump 41, in combination with the valve 27, maintains low pressure in the microwave cavity 29 and line 33. A photodetector 44 detects the light in the monochromator and the results are recorded on the recorder 51. It is preferred that oxygen from a source 33 also be admitted into line 31. The oxygen serves to burn off deposits of sulfur, carbon and phosphorous and carry these elements out of the tubing to prevent contamination from a possible residue thereof. Figures 2-4 disclose the linearity of the results obtained utilizing an exponential dilutor or a known amount of a given material being admitted over a time period to the discharge region. These figures serve to illustrate the point that once the device is calibrated for a given point for a known element one can then utilize any sample containing that element present in any material. The ampere reading is directly proportional to the amount of the element present. For example, once a given point is determined for a known amount of an element such as C in CO, in

in the readout of the apparatus of the herein invention on a graph such as shown in FIGS. 2-4, then if twice the amperage readout is obtained one will know that for the same compound, CO, twice the amount of the compound is present. Alternatively, if a different compound, C_2S , containing twice the amount of the element C is present and the amperage is doubled then the same amount of the element is present as was in the calibrated material, since the output is strictly a linear function.

It can thus be seen that the herein device and method provides for a very effective and simple means for exactly determining the amount of an element present in a sample of a given material. One can relate the amount of element present to the amount of a particular compound in the sample. The calibration of the device is very simple, and once calibrated can be utilized for determining the presence of a given element regardless of the type of material passing through the apparatus containing that element. Such advantages were heretofore not present in prior art techniques and devices.



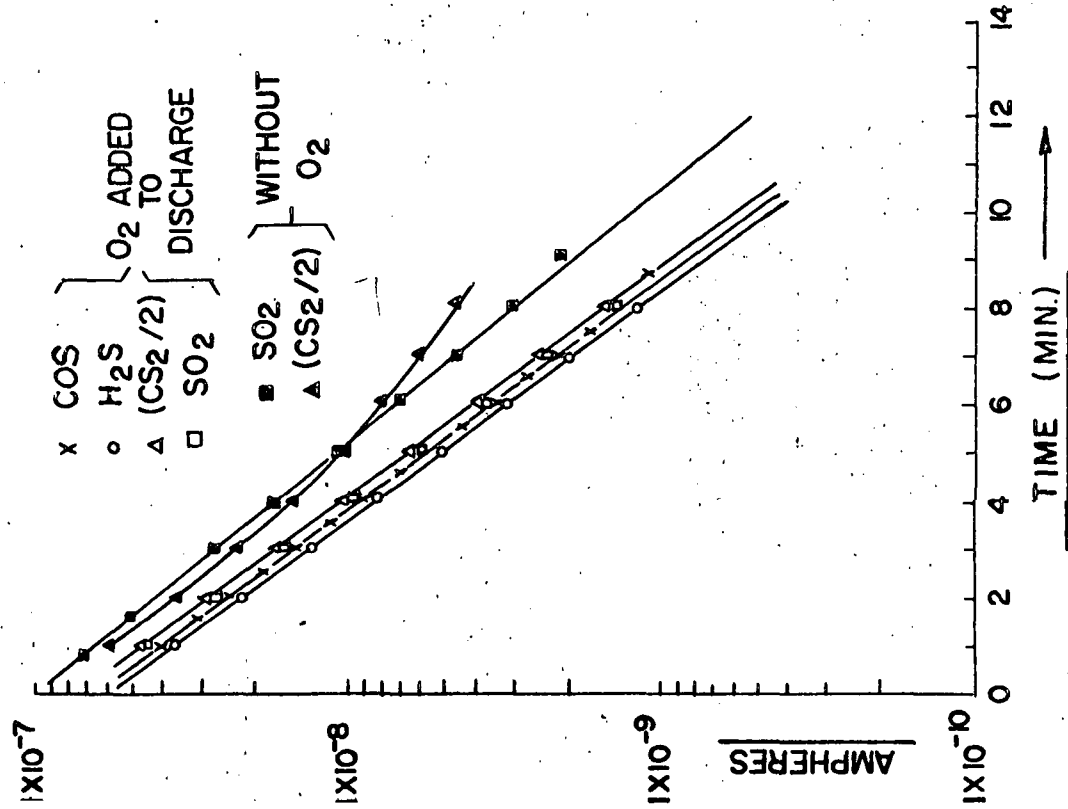


FIG. 2

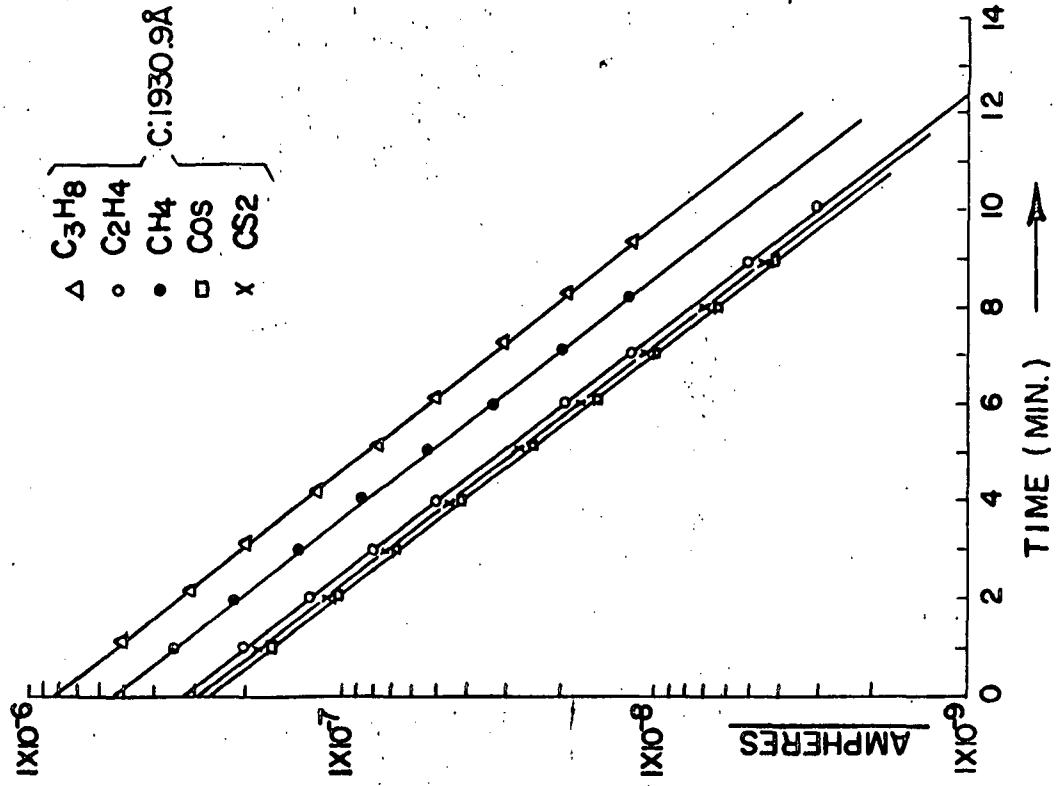


FIG. 3

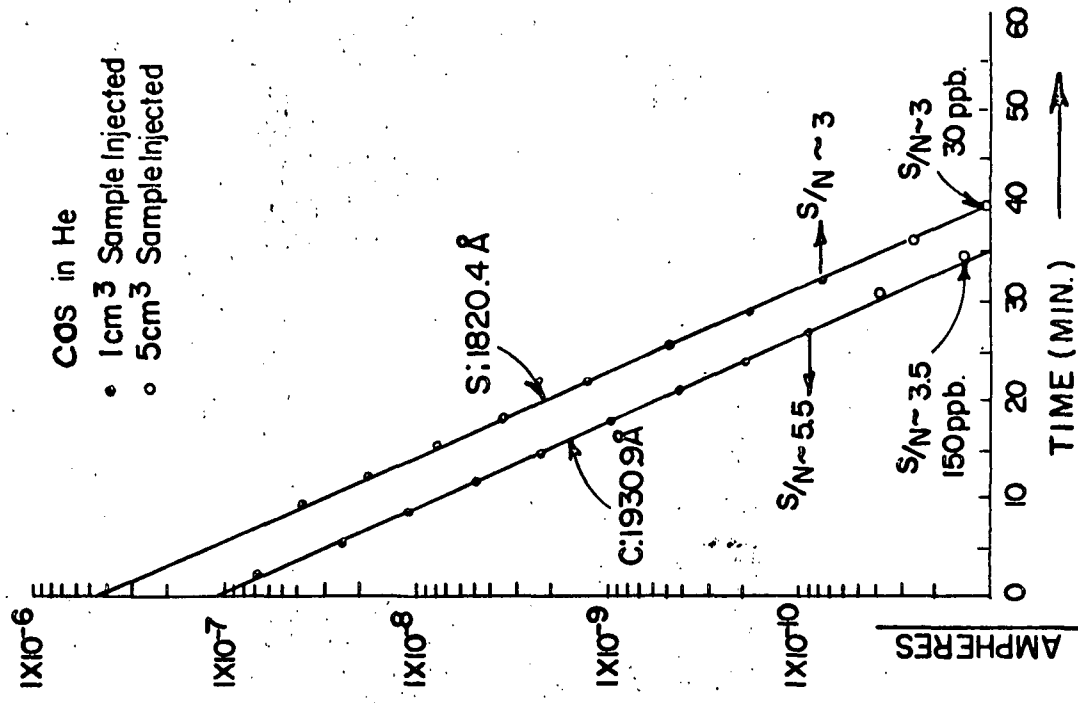


FIG. 4

BACKGROUND OF THE INVENTION

1. Field of the Invention:

This invention is in the field of analysis of compounds. More particularly the invention relates to a device and method for the quantitative and qualitative chromatographic analysis of elements in compounds.

2. Description of the Prior Art:

Atomic and molecular emission detection has been widely utilized in gas chromatographic applications. Such detection methods are highly sensitive and frequently quite selective. The technique of atomic and molecular emission detection consists of introducing effluents from chromatographic columns containing trace quantities of compounds into a discharge. The discharge is excited either by means of microwave power or high voltage d.c. or a.c. In the discharge, the compound is fragmented by electron bombardment and by collision processes involving rare gas metastable species to produce electronically excited atoms as well as electronically excited diatomic fragments. Emissions from these species have been isolated by means of a monochromator and used to detect the presence of a compound in the effluent rare gas stream. Thus, the emitted spectral wavelength has frequently been an indication of the elemental composition of the effluent compound. In the past, various methods of producing discharges, the nature of the rare gas utilized, column materials, pressure conditions and other parameters have been investigated in order to evaluate the linearity, sensitivity, and selectivity of this type of detection

1 method.

2 It should be particularly pointed out that in most
3 prior art approaches, high gas pressure was utilized to ana-
4 lyze for compounds as compared to the analysis of particular
5 elements in compounds. Such methods relied upon chemical
6 reactions to transpire which produced compounds that were
7 observable, particularly in the visible and near visible
8 ultraviolet region. Such methods were thus not able to make
9 linear quantitative analyses, particularly because of their
10 reliance upon such chemical reactions. Thus, heretofore, no
11 method had been successfully devised for quantitatively and
12 qualitatively determining the presence of elements in effluent
13 gases.

14 More particularly, the first systematic investigation
15 in the prior art of UV-visible atomic emission chromatographic
16 detection involved selective analysis of drugs and pesticide
17 residues which was demonstrated by using the most intense
18 phosphorous, sulfur, chlorine, bromine, and iodine lines in
19 the UV-visible spectrum. In addition to achieving sensitive
20 and highly selective qualitative detection, workers were
21 also able to attain a fair degree of linearity of detector
22 response for different organic compounds containing various
23 amounts of a given element and different types of chemical
24 bonds. This was achieved by analyzing very small concentrations
25 of a sample and by employing high power densities in a capillary
26 discharge lamp. Reasonably intense atomic emissions were
27 achieved through the use of a helium carrier gas. It should
28 be pointed out, however, that the prior art methods did not
29
30
31
32

1 involve detection in the vacuum UV region nor did they involve
2 the quantitative and qualitative detection of specified ele-
3 ments.

4 Molecular fragment detection, as compared to atomic
5 detection, has been obtained under high pressure conditions
6 by additional workers in the prior art. Such molecular frag-
7 ment detection appears to be one hundred to one thousand
8 times more sensitive than atomic emission detection. However,
9 the molecular emission detection is frequently not linear and
10 requires separate calibration for each compound. Further,
11 sensitivity varies markedly with the type of fragment emission
12 measured and frequently requires the presence of impurities
13 in the discharge such as nitrogen to obtain CN emission from
14 hydrocarbons. Thus, for quantitative purposes, atomic emission
15 is more useful in spite of lower limits of detection possible
16 by other means.

17 SUMMARY OF THE INVENTION

18 The herein invention provides a device and method for
19 performing qualitative and quantitative elemental analysis
20 through the utilization of a vacuum UV chromatographic detector.
21 In the herein invention, a carrier gas, such as helium is
22 utilized at a low pressure. The carrier gas carries a sample
23 to a gas chromatographic column. The output from the column
24 is then directed to a microwave cavity where a low pressure
25 microwave discharge produces fragmentation of the compounds
26 present and generates intense atomic emissions in the vacuum
27 ultraviolet. The emissions are then directed into a vacuum
28 ultraviolet monochromator. The monochromator is tuned to the
29
30
31
32

1 wavelength of a particular element that is known to be present
2 in the sample. The intensity of the spectral component is
3 proportional to the amount of element present in the sample.
4 When the apparatus is calibrated by initially running a known
5 sample of material therethrough and analyzing it, one can
6 obtain a linear readout for any compound containing that
7 element utilizing the foregoing device and process. It is
8 preferred to additionally mix a small amount of oxygen with
9 the output of the column prior to the output reaching the
10 microwave cavity. The oxygen will break down in the presence
11 of the microwave cavity and react with elements such as carbon,
12 sulfur, or phosphorous, burning them out of the walls of the
13 apparatus so that they cannot further contaminate the apparatus
14 or poison the material in the microwave cavity. Thus, it can
15 be seen that the herein device and method can be made absolute
16 and has a linear response over a wide concentration range of
17 material. By absolute it is meant that one can calibrate the
18 device initially by using a standard sample of a material that,
19 for example, contains an element such as carbon. Once this
20 calibration is made, then one can measure any carbon-containing
21 compound coming through the apparatus to determine the quantity
22 of the carbon present. This results from the fact that the
23 signal generated from the monochromator is directly proportional
24 to the number of carbon atoms present. It is believed that
25 the invention will be further understood from the following
26 detailed description and drawings in which:

27 BRIEF DESCRIPTION OF DRAWINGS

28 FIG. 1 is a schematic representation of the device of
29
30
31
32

1 this invention.

2 FIG. 2 is a plot of current (amperes) vs. time for
3 various sulfur containing compounds analyzed by this invention.

4 FIG. 3 is a plot of current (amperes) vs. time for
5 various carbon containing compounds analyzed by this invention.

6 FIG. 4 is a plot of current (amperes) vs. time for
7 carbon and sulfur from a COS sample analyzed hereunder.

8 DESCRIPTION OF THE PREFERRED EMBODIMENT

9 Attention is now directed to the schematic diagram of
10 FIG. 1 which shows an arrangement of apparatus utilized to
11 perform the novel method of the herein invention. A source of
12 helium 11 is provided. The helium is monitored through a
13 valve 13 to control the pressure of the gas emitted into a line
14 15. From line 15 the helium passes through a molecular sieve
15 in a liquid nitrogen trap. A preferably five angstrom molecular
16 sieve is utilized which is cooled to a liquid nitrogen temper-
17 ature by the trap. The purpose of the molecular sieve is to
18 remove trace carbon and nitrogen impurities such as CO, N₂,
19 CO₂, and H₂O from the helium carrier gas. An outlet line 19
20 from the molecular sieve is directed to an area 21 which can
21 be occupied by either an exponential dilutor for calibration
22 of the device or a gas chromatographic column when an analysis
23 is being made. Intersecting line 19 prior to the dilutor or
24 column 21, is a sample injection port 23 which admits a sample
25 of the material being analyzed into the helium gaseous stream.
26 Thus, the sample is either diluted exponentially by a dilutor
27 at 21 or separated into its components by a chromatographic
28 column, if such occupies 21. The difference between the uti-
29
30
31
32

1 lization of the dilutor for calibration and the column for
2 the actual running of an analyzation of an unknown sample will
3 be explained in further detail. The output from either the
4 dilutor or column 21 is directed through an output line 25
5 through a needle valve 27 which serves to control the pressure
6 in a microwave cavity 29. The helium particularly serves also
7 to dilute the sample being analyzed to a low enough concen-
8 tration to assure 100 percent decomposition in the microwave
9 cavity. The concentration of the sample should be about one
10 part in 10,000. The lines for carrying the gas up to needle
11 valve 27 may be glass or metal, so long as they are nonreactive
12 and will not contaminate the material passing therethrough.
13 Line 27 then continues to the microwave cavity area 29. An
14 area 31 between the needle valve 27 and the microwave cavity
15 should preferably be of quartz tubing or cooled glass because
16 of the high temperature inside the microwave cavity.

17 The device is additionally preferably provided with a
18 source 34 of oxygen which can be directed through line 36 pass-
19 ing through a needle valve 38 to intersect the line 25 just
20 downstream of the needle valve 27 so that a small amount of
21 oxygen can be mixed with the gas entering line 31 preceding
22 the microwave cavity 29. The needle valve 38 in the oxygen
23 line 36 serves to also control the total pressure in the micro-
24 wave cavity. As indicated, the oxygen will react with S, C,
25 or P and burn and carry these elements out of tubing to prevent
26 contamination from a possible residue of these elements.

27 At the microwave cavity 27 the helium discharge is
28 excited. It is preferred to utilize a high frequency microwave
29
30
31
32

1 unit on the order of 2450 MHz. It is important that the
2 microwave unit used does not have electrodes in the tube
3 because of the possibility of introduction of impurities
4 from the electrodes into the discharge. Thus, a diathermy-
5 type microwave unit should be utilized. It is particularly
6 desirable to use a low pressure microwave discharge in order
7 to obtain complete dissociation. Such relates to maximizing
8 energy coupling of the microwave to the gas and obtaining
9 a high energy density. A line 33 is connected between the
10 microwave cavity 29 and a window 35 of a monochromator 37.
11 The window, for example, can be lithium fluoride or other
12 similar vacuum ultraviolet transmitting material. The win-
13 dow material will be selected depending upon the region of
14 the spectrum being analyzed. Thus, MgF, quartz and the like
15 can be used depending upon the low wavelength cutoff point.
16 The connection between the line 33 and the window 35 is a
17 vacuum coupling preferably as disclosed in U. S. Patent
18 3,493,805 wherein an arrangement for connecting the output
19 from a microwave source to a window by means of such a vacuum
20 connection is shown. Intersecting line 33 is a line 39
21 which is connected to a suitable mechanical pump 41 which
22 serves to withdraw the gas from the system. A throttle valve
23 43 in line 39 serves to maintain the desired low pressure in
24 the range of 1 to 20 mm of mercury in the microwave cavity.
25 The pressure in the microwave cavity can be measured precisely
26 by a pressure gauge 45. The volume flow of gas through the
27 microwave cavity can be monitored by venting the exhaust of
28 the mechanical pump 41 through a soap bubble flow meter not
29 shown.

1 The output of the monochromator can be taken through
2 a photomultiplier (having for example a CsTe photocathode)
3 which is connected to a small exit slit in the monochromator.
4 The photomultiplier tube 44 is connected to a regulated high
5 voltage supply 47 which serves to amplify the photocurrent
6 produced in this tube by the impinging photons. Additionally,
7 the photomultiplier tube is connected to an electrometer 49
8 and recorder 51 which in turn is connected to the electrometer.
9 The electrometer serves to amplify the current produced in the
10 photomultiplier tube to a level which can be displayed on the
11 recorder. Background signals from the helium gas flowing
12 through the microwave cavity can be subtracted out using an
13 electrometer offset circuit. The electrometer offset circuit
14 produces a negative signal which can be adjusted to precisely
15 balance out the background signal from the discharge and from
16 the photomultiplier dark current.

17 In the utilization of the apparatus depicted in FIG. 1,
18 a vacuum monochromator 37 was chosen which would isolate
19 atomic-lightwave length positions below 2,000 Å. Various
20 intense atomic line spectral positions and electronic transi-
21 tions appearing in the vacuum UV have been previously determined
22 and tabulated. Thus, in the tests of the herein invention,
23 the carbon 1930.9 Å line was used to monitor carbon containing
24 compounds, 1742.7 Å line for the nitrogen containing species,
25 and the 1826.3 Å sulfur line was used for sulfur. For the
26 determinations with the apparatus an entrance slit setting of
27 about .05 mm was utilized for the monochromator while the
28 photomultiplier used to measure the line emissions was connected
29
30
31
32

1 also to a .05 mm slit in the monochromator.

2 Example I

3 In this example, a dilutor is utilized as element 21
4 in the apparatus of FIG. 1. The dilutor particularly uti-
5 lized in this example is known as Lovelock exponential dilutor
6 described by J. E. Lovelock, in Analytical Chemistry, 33 (1962)
7 162. The dilutor was operated at 1 atmosphere of pressure of
8 helium. The inlet to the microwave cavity 29 was adjusted
9 so that the pressure in the discharge region was about 2 mm
10 Hg total pressure. At this pressure, a stable discharge
11 through helium can be maintained. The microwave cavity was
12 about 10 cm from the entrance slit of the monochromator and
13 the discharge took place in a 10 mm I.D. quartz tube portion
14 33 which was viewed end-on through the lithium fluoride window
15 35. The microwave unit was a tuneable Evenson microwave cavity
16 as described in Review of Scientific Instruments, 36 (1965)
17 294.

18 With the exponential dilutor in line with the microwave
19 cavity, an injected sample through port 23 was diluted at a
20 constant rate with helium and the response at a particular
21 spectral position was monitored as a function of a known con-
22 centration of the sample passing through the lamp section.
23 The dilution was calculated from

24 1.
$$C = C_0 \cdot e^{-Kt}$$

25 where C is the concentration at time T; C_0 , the concentration
26 at $T=0$; and the constant K, obtained from slope of a semilog
27 plot of C against t, is related to the volume of the dilution
28 flask V (CM^3), and the volumetric flow rate, ϕ ($\text{cm}^3 \text{sec}^{-1}$), through

29 2.
$$K = \phi/V$$

30

31

32

1 Both V and ϕ can be accurately measured. If the response
2 of the detector is truly linear with the concentration of sample
3 exiting from the dilution flask, then a linear plot of $\log(s)$
4 vs. t is obtained where S is the photomultiplier current and
5 the value of K obtained from the slope will agree with the
6 value of K calculated from eqn. 2.

7 A plot of the log of photomultiplier currents against
8 time according to equation 1 above should yield a straight
9 line plot. Linear behavior on a semilogarithmic plot in itself,
10 does not demonstrate detector linearity unless the slope agrees
11 with that obtained through equation 2.

12 FIG. 2 displays the linearity of the detector response
13 using the sulfur 1826.3 Å emission line for various sulfur
14 containing compounds including COS, H₂S, SO₂, and CS₂. In
15 FIG. 2, the initial sample size for each compound was 4×10^{-9}
16 moles. The figure, additionally, shows the effect of oxygen
17 added to the discharge, as seen from the lower family of curves.
18 The absence of oxygen, as indicated in the upper two curves,
19 shows nonlinear behavior. Further, the slope for sulfur atom
20 response without added oxygen is considerably lower than the
21 value calculated from the volume of the dilution flask and the
22 helium flow rate. Sulfur polymers it is believed, deposit on
23 the walls of the microwave cavity and are removed very slowly
24 thus accounting for a delayed response and smaller slope. The
25 effect is much more pronounced for CS₂ than for SO₂ and distinct
26 curvature can be noted on the semilogarithmic plot of FIG. 2.
27 A distinct light brown film was observed to develop over long
28 operating times. After operating the lamp without oxygen for
29
30
31
32

1 some time, addition of oxygen to the discharge was found to
2 cause a rapid removal of the deposit with a sudden development
3 of a very large sulfur atom emission signal. By continuously
4 passing oxygen through the discharge no deposit forms and the
5 response to the sulfur number in the parent compound is linear.
6 The relative response of the signal is approximately the same
7 for COS, SO₂, H₂S, and CS₂/2 as shown by the lower family
8 of curves in FIG. 2. The total spread of these curves, which
9 was about 10%, is in general agreement with the precision of
10 preparing the standard mixtures and sampling.

11 FIG. 3 demonstrates the potential linearity for various
12 carbon compounds. The curves were developed with an oxygen
13 flow maintained utilizing the set up of FIG. 1 with an exponential
14 dilutor in the same manner that the curves of FIG. 2 were de-
15 veloped. As found for the sulfur compounds shown in FIG. 2,
16 the slopes for the carbon compounds agree with the value calcu-
17 lated from the volume flow and the volume of the dilutor.
18 The relative response additionally appeared to be independent
19 of the carbon containing compound but follows closely the
20 number of carbon atoms in the compound. That is, equal amounts
21 of CH₄, C₂H₄, and C₃H₈ gave responses in the ratios of 1:2:3.
22 Deviations from linearity were also observed as in the sulfur
23 case, although the deviations were somewhat less pronounced.
24 Non-linearity in signal vs. the carbon atom number in the
25 carbon compound was observed in the absence of supplementary
26 oxygen flow. Such deviations from linearity were severest
27 for the higher molecular weight hydrocarbons. In forming
28 FIG. 4, the initial sample size was the same for each
29
30
31
32

1 measurement which was 4×10^{-9} moles.

2 It should be pointed out that the dilutor is used to
3 demonstrate the linearity of the herein apparatus since there
4 are varying concentrations of the sample put out by the
5 dilutor. Rather than using the dilutor, one could calibrate
6 the device through the use of a sample of a known concen-
7 tration.

8 Example II

9 When a chromatographic column replaces the exponential
10 dilutor at position 21 of FIG. 1, samples were prepared by
11 utilizing a gas syringe of 1 ml volume filled to atmospheric
12 pressure with a particular compound. The material from the
13 syringe was injected into an exponential dilutor, which was
14 external to the entire detection apparatus, at the helium
15 inlet side through a T-fitting equipped with a rubber septum
16 seal. At set time intervals, 1 and 5 ml samples were extracted
17 from the exit side of the dilutor which was vented to the
18 atmosphere. These samples that were extracted were then
19 injected into the injection port inlet to a gas chromatographic
20 column. In this manner, chromatograms were developed for
21 large variations and sample size and the absolute concentrations
22 could be estimated from the known or measured flow rate to
23 the dilutor and the volume of the dilution flask which was
24 300 cm^3 . Linearity of the detector in the chromatographic
25 mode of operation was again verified by plotting the
26 logarithm of the peak height versus time, and comparing the
27 slope with the calculated slope attained from equation 2
28 above, using the flow rates or the dilution flask. Mixtures
29
30
31
32

1 of two or more compounds were prepared in sample flasks
2 equipped with a rubber septum at known dilution in helium.
3 These were samples at atmospheric pressure with a 1 ml
4 syringe and injected into the chromatograph.

5 Though several column materials can be utilized in
6 the chromatographic column, depending upon the compounds
7 investigated, the majority of experiments were performed
8 utilizing Porapak-N made by Waters Associates (Framingham,
9 Mass.) in a 1/4 inch by one foot long stainless steel column.
10 The results indicated below are with this particular column
11 material. Other column packing materials that give good
12 results include a molecular sieve, silica gel and crushed
13 fire brick treated with squalane. The column temperature was
14 controlled by means of a water bath, whose temperature was
15 measured by a mercury immersion thermometer. Employing a
16 $160,000 \text{ cm}^3 \text{ sec}^{-1}$ mechanical pump, unthrottled, and maintaining
17 about 1-2 Torr pressure in the microwave cavity section of the
18 detector resulted in flow rates of about $200 \text{ atm cm}^3 \text{ sec}^{-1}$
19 through the chromatographic column. The pressure in the column
20 was slightly over 1 atm which was also essentially the same
21 pressure in the dilutor when it was utilized in the apparatus.

22 FIG. 4 indicates the linearity of the chromatographic
23 column in the detection system of this invention. Samples
24 of COS were taken as a function of time from the exponential
25 dilutor. They were injected into the chromatographic injection
26 port and the peak heights measured in amperes were plotted
27 on semi-log paper. Both carbon and sulfur atomic emissions
28 were monitored. The carbon atomic emission was at $1930.9 \text{ \AA}.$
29
30
31
32

1 The sulfur atomic emission was at 1820.4 \AA . The helium flow
2 rate in the exponential dilution flask was $90 \text{ cm}^3/\text{minute}$.
3 The volume of the flask was 300 cm^3 . The initial injection
4 was $.5 \text{ atmosphere-cm}^3$ of COS into the mixing flask. The
5 photomultiplier dynode voltages were 2.5 kV and 3.0kV for
6 the C and S respectively. This test of linearity examined
7 not only the detector linearity but also the sampling from
8 the dilutor plus the column. Once again, as in the previous
9 example, the K obtained from the slope agrees within several
10 percent of the value calculated from equation 2 using the
11 flow rate through the dilutor and the dilutor volume. The
12 range of linearity appears to be at least four orders of
13 magnitude, ranging from large sample sizes of 10 Torr cm^3 to
14 sample sizes less than $10^{-3} \text{ Torr cm}^3$.

15 It appears that the detection limit of the present
16 apparatus, sampling at the lowest concentration limit with
17 a 5 ml injection syringe, is about 100 p.p.b. for carbon and
18 30 p.p.b. for sulfur. The limit, for this instrument, is
19 arbitrarily fixed as a measurement which can be made at a
20 signal to noise ratio of 3:1. Sulfur determinations are
21 somewhat more sensitive than carbon because of a lower back-
22 ground level for sulfur than for carbon with only "pure" helium
23 flowing through the microwave cavity.

24 It can be seen from the above examples and discussion
25 that the herein method and device provides an accurate
26 determination of the quantity of an element present in a gas
27 sample. In Example I, the dilutor was particularly utilized
28 to demonstrate the linearity of the herein method. The
29
30
31
32

1 linearity of course, is reflected in the results shown in
2 FIGS. 2-4. As a practical matter, the system can be readily
3 calibrated for a given element by merely running a sample
4 of a known concentration of a given material through a column
5 and obtaining a reading from the monochromator. For example,
6 one can insert into the system a known amount of carbon dioxide
7 and obtain a given reading from the monochromator in terms
8 of ampere output. Once this has been done, successive samples
9 of carbon containing compounds can be readily qualitatively
10 measured. For example, if an unknown example of carbon monoxide
11 contained twice as much of that material than that used for
12 the calibration then the reading from the monochromator would
13 indicate twice the current (amperes). Likewise, if a compound
14 containing twice the carbon atoms such as C_2H_4 was measured
15 and this material was present in the same amount as the cali-
16 bration sample, then once again, the readout would be twice
17 the current (amperes) as the calibration sample. In other
18 words, the same reading will be obtained for twice the amount
19 of CO_2 or the same amount of C_2H_4 since in each instance there
20 are twice as many carbon atoms present as the calibration
21 sample referred to. By utilizing the gas chromatographic
22 column one, of course, will know whether the readout at a
23 given instance in time is CO_2 or C_2H_4 or some other carbon
24 containing compound and thus can relate the ampere reading to
25 the amount of carbon present or in turn the amount of the compound
26 containing the carbon present. Thus, heretofore, there has
27 not existed a system which will provide such an accurate
28 qualitative determination of material based upon a single
29
30
31
32

1 calibration. In past systems, a separate calibration was ne-
2 cessitated for each differing compound to be analyzed. In
3 the present system one merely makes a single calibration for
4 each element to be analyzed in that system. One then can
5 determine the amount of that element present in any compound
6 containing it that passes through the system.

7 Not only will the present system provide an indication
8 of elements such as N, Br, I, P and the like. Oxygen and
9 hydrogen analysis are possible in the present system, but
10 require utilization of spectral emission lines in the visible
11 region rather than the vacuum ultraviolet region of the spectrum.

12 Applying the principles of the herein invention, it
13 can be seen that this device can be used to determine the
14 elemental composition of an unknown peak in the gas chromato-
15 gram. If the unknown peak is due to a chemical compound, the
16 atomic ratios in the compound can be determined. By injecting
17 repeated samples of uniform size, the calibrated detector can
18 be used to measure relative signals for each element contained
19 therein. The relative signals adjusted for response of
20 standard samples are in the ratios of the atomic composition.